

# analysis



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## AN EDITORIAL NOTE:

Laboratory people tend to consider themselves as somewhat special. Special in the sense that laboratory work has always possessed an aura of mystery and excitement, of searching and striving for the unknown. By association in the minds of the public, laboratory workers have inherited that "special status" designation. They have been likened to white-coated acolytes, silently moving in a mysterious world of glass and instruments, ceaselessly seeking to wrest new secrets from nature.

The romantic image and the reality are quite different, of course, especially in an environmental analytical laboratory. Routine analytical work has a goodly component of drudgery and repetition, of exacting requirements which leave little scope for the imagination. Yet the sense of challenge can be found even in the most mundane analytical task. Improving the precision and accuracy of a test, overcoming interferences in a procedure, or generating numbers which have relevance and upon which environmental actions and strategies are based, these activities will continue to give a sense of achievement and satisfaction.

Environmental analytical laboratories can be considered a key part of an "early warning system" for monitoring the environmental well-being of a community. The work carried out in environmental laboratories has the added virtue of being relevant to the life-style of the surrounding community. In times of economic constraints, research and scientific programs traditionally have tended to be vulnerable targets for cut-backs. We are living in a more perceptive age now, and we can only hope that when decisions are being made concerning program priorities, the value and importance of the research and analytical programs will not be lost sight of.

As the eyes are the windows to the soul, laboratories can be perceived as the windows to the environment. To protect the environment, it is essential to know man's impact on ecosystems. This is the task and responsibility of the environmental scientists. Given the necessary support, the scientific community can continue to define the nature of environmental ills and prescribe new directions for protecting and enhancing the quality of the environment.

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## THE ANALYSIS OF THE CONTENTS OF WET PRECIPITATION COLLECTORS FOR METALS

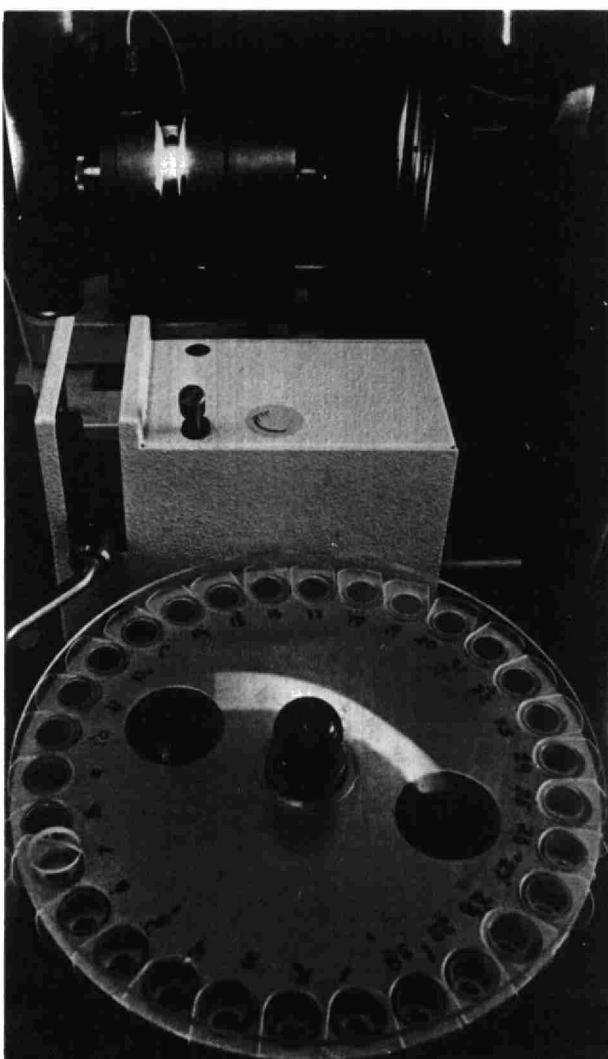
Since the completion of the Sudbury superstack there has been increasing concern about the degree, nature and distribution of acid rainfall in Ontario. In order to gain some understanding of the situation, staff involved in the Sudbury Environmental Study placed several Wet Precipitation Collectors (WPC) at varying distances and directions from Sudbury.

A WPC is basically a plastic drum of about 25 cm diameter and 45 cm depth equipped with a lid controlled by a moisture sensing device and servo motor such that the drum is uncovered at the onset and closed at the cessation of precipitation. The containers are left in the field for one month, then sealed and shipped to the laboratory.

The accurate estimation of the trace metal content of the precipitation initially presented the laboratory with several analytical problems. Since the most important single parameter of the rain or snow collected was pH, acid preservation of the collector contents was not possible. Preliminary controlled laboratory experiments showed that up to 50% of the initial concentration of certain elements, such as iron, was lost to the container walls over 30 days. Metal levels are typically less than 50 ug/l, except for iron. Also, because of the extensive parameter list, sample volume was usually not sufficient to employ the routine low level technique of preconcentration by evaporation followed by flame AAS.

The following scheme was devised to overcome these difficulties. Upon receipt at the laboratory a 25 ml aliquot is removed from the sample and is immediately acidified. The remainder of the sample is then taken and analyzed for the required water quality parameters. The sample is then analyzed for Fe, Cu, Al, Cr, Ni, Pb, Zn and Cd by flameless AAS technique admirably suited for this situation because of its sensitivity of 1 ug/l or better for most elements and its very low sample volume requirements (20 ul/analysis). The container is then leached with 5% nitric acid which serves the dual purpose of

cleaning the container and extracting any adsorbed metals from the container walls. The acid extract is analyzed for iron, chromium and aluminum. These elements were selected because controlled laboratory studies had shown them to be susceptible to adsorption under the field conditions, and this was corroborated by real sample field data.



The leachate values, when combined with the analyses of the collector contents and volume factors, provide an accurate measure of the amount of heavy metals carried into the containers by rain or snowfall.

The program to date has been characterized by excellent laboratory-field cooperation and communication which greatly facilitated our efforts to devise a solution to a difficult analytical problem.

(B. Loescher - (416) 248-3346).

## ISOLATION AND DETECTION OF KLEBSIELLA PNEUMONIAE AND PSEUDOMONAS AERUGINOSA IN PULP AND PAPER MILL WASTES

Several rivers in Southern Ontario are heavily contaminated with fecal bacteria. The contamination in many cases is from non-point sources and therefore difficult to trace, but in some cases large point sources of pollution have been clearly identified. A study in 1977 discovered a large input of fecal bacteria in pulp and paper-mill wastes which was discharged to the Sturgeon River at Sturgeon Falls.

Established analytical techniques capable of determining fecal coliforms in water that has been contaminated with sewage, cannot be routinely applied to water which has been contaminated with certain industrial wastes such as those from the pulp and paper-mill industry.

The main problem stems from the fact that some bacteria of non-fecal origin grow with and appear similar to the fecal coliforms. The solution adopted in this survey was to purify and identify a representative sample of the fecal coliform colonies.

A pathogenic bacterium, Klebsiella pneumoniae, was identified as the principal fecal coliform discharged into the Sturgeon River. K. pneumoniae has been associated by others with pulp and paper-mill wastes (Huntley, Jones, and Cabelli 1976). In addition, another pathogen, Pseudomonas aeruginosa, was identified and found in substantial numbers in the pulp-mill wastes. P. aeruginosa has not been reported in pulp and paper wastes before. The significance of the presence of these pathogenic bacteria in the river water is under further investigation.

(G. Hendry - (248-3008).

Laboratory scientists have put together a Guide to the Collection and Submission of Samples for Laboratory Analyses. Write for a copy to the Water Quality Section, Laboratory Services Branch, P.O. Box 217, Markdale, Ontario, N0R 1L1.

## SPECIFICITY OF mENDO LES AGAR AND EMB AGAR

In a continuing effort to upgrade and evaluate bacteriological procedures, the Microbiology Section has been conducting studies on new media for the isolation and enumeration of Escherichia coli and Klebsiella pneumoniae.

As part of these studies, two established Total Coliform media, mENDO LES Agar and Eosin Methylene Blue (EMB) Agar, were also tested. On a series of samples from various sources, both target and non-target colonies have been picked and subjected to purification and identification procedures.

The results of the identification have shown that neither media can be reliably used in procedures designed to indicate fecal pollution.

One hundred and thirty-one target organisms were isolated from 12 samples analyzed using EMB and of these only 47 were Enterobacteriaceae. Of the 47 only 6 were E. coli and 21 were Klebsiella sp. The largest proportion of target organisms consisted of 63 cultures of Aeromonas sp. and 15 cultures of Acinetobacter sp. Of the 106 non-target colonies identified, 36 were Enterobacteriaceae of which 4 were E. coli and 2 were Klebsiella sp.

Eighty-five target colonies were isolated from mENDO LES Agar. Of the 85, there were only 49 Enterobacteriaceae including 15 E. coli and 26 Klebsiella sp. Again the largest single occurring genus was Aeromonas with 33 cultures isolated. The 75 non-target colonies included 27 Enterobacteriaceae of which one was an E. coli (no Klebsiella sp. were isolated).

The results obtained demonstrate that neither medium is specific enough for a Total Coliform determination, let alone for E. coli. Furthermore, the identifications that have been done indicate that fluctuations in "Total Coliform" counts obtained with these media would be responsive to increases in bacterial inputs from many sources, not just fecal material, and therefore these total coliform counts should not be used as a measure of fecal pollution.

(M. Young - (416) 248-3008).

## THE DETERMINATION OF CYANIDE BY GAS CHROMATOGRAPHY

The cyanide ion is found in effluents from metal plating and pickling operations, and is very toxic to many forms of terrestrial and aquatic life. The laboratory annually performs about 2000 cyanide analyses using a cumbersome colourimetric procedure involving the use of potentially hazardous chemicals such as barbituric acid and pyridine. Recently, however, a simple, rapid, and sensitive gas chromatographic method has been adopted by the laboratory for routine cyanide analyses. The method is based on the formation of cyanogen bromide which is strongly electron capturing. Samples can be directly injected in aqueous solution and very low levels of cyanide can be detected using relatively simple gas chromatography equipment.

The most common application of the method is the determination of "total" cyanide, in which a water sample that has been preserved with sodium hydroxide is acidified, then distilled into a basic solution which traps the evolved hydrogen cyanide. During the distillation, metal-cyanide complexes (such as ferricyanide, ferrocyanide, and cuprous cyanide) are broken down, so that the distillate contains the total amount of the cyanide ion present in the sample aliquot. An aliquot of the distillate is taken, and acidified with phosphoric acid. The sample aliquot is then treated with a few drops of bromine water. The bromine reacts with the cyanide ion to form cyanogen bromide. The reaction is virtually instantaneous, and after the excess bromine is reacted with aqueous phenol, the solution is directly injected into a gas chromatograph. The detection limit is 2 ppb for total cyanide.

The same procedure can also be applied to an undistilled aliquot of the sample to obtain "free" or non-complexed cyanide content, as well as for determining thiocyanate. The thiocyanate ion also reacts with bromine to form cyanogen bromide. Therefore, the treatment of an undistilled sample with phosphoric acid, bromine water, then phenol yields a combined thiocyanate-cyanide result. The final step involves obtaining a result for thiocyanate only. Prior to acidification, 0.5 ml of a dilute formaldehyde solution is added to a duplicate 3 ml aliquot of a sample. In basic solution, cyanide ion reacts with formalde-

hyde to form a cyanohydrin that is resistant to the mild bromine oxidation. A small portion of the formaldehyde-treated aliquot is then injected into a GC to produce the thiocyanate value. The free cyanide can then be obtained by the difference in the two results.

This gas chromatographic procedure has numerous advantages: it is very fast, requiring less than 15 minutes for a free cyanide analysis, uses an extremely simple procedure, requires a very small sample aliquot, and is virtually free of interferences.

(B. Neary - (426) 248-3775)

## SEMI-AUTOMATED PROCEDURE FOR THE DETERMINATION OF LOW LEVELS OF TOTAL MANGANESE

Total manganese is determined in water samples by a two-stage system: batch digestion followed by automated colorimetry. Manganese is solubilized by autoclaving in an acid-reducing medium at 121°C for one hour. Samples taken directly from the digestion tubes are analyzed by the Technicon AutoAnalyzer II System. The colourimetry is based on the formation of the manganese-formaldoxime complex. Cation interference, especially ferrous ion, is controlled by the use of four complexing agents while sample-colour interference is eliminated by using a blanking stream which is synchronized with the colour stream. Both streams receive identical quantities of reagents, but the order of addition is altered in the blanking stream to prevent the formation of the manganese-formaldoxime complex.

In the range of application (0.006 - 0.200 mg/L Mn) the accuracy and precision of the method are comparable to those of flame atomic absorption spectroscopy (AAS). Cost and increased productivity as well as a lower detection limit (order of magnitude) favour the colourimetric method. Moreover, since the same digestion procedure is suitable for total iron analysis, both parameters are determined simultaneously by means of a dual-channel AutoAnalyzer system.

(J. Crowthers - (416) 248-3512)

## PSEUDOMONAS AERUGINOSA AND EAR INFECTIONS

Each year numerous swimmers experience ear infections after bathing in recreational waters. The most common ear infection, otitis externa or "swimmers' ear", is usually associated with the bacterium Pseudomonas aeruginosa and often requires medical treatment to overcome the painful symptoms. In an attempt to assess the health significance of water-borne P. aeruginosa and to investigate the relationship of this bacterium to ear infections among swimmers, the Lakeshore Capacity Study Microbiology Component conducted a pilot epidemiology study at two recreational lakes in the Muskoka District last year.

The study was carried out during the summer months and involved cottagers at Muskoka Bay, children in swimming classes at Gull Lake Park and physicians in the Town of Gravenhurst. The cottagers and swimmers were surveyed for information concerning their past and present histories of swimming activity and ear infection. The ears of these participants were swabbed on several occasions and tested for P. aeruginosa. The shoreline waters and sediments were also intensively sampled to determine the distribution of P. aeruginosa. Ear cultures from otitis externa patients were obtained from local physicians. All isolates of P. aeruginosa from these specimens were retained and further characterized by specific serological and phage-typing procedures.

At Muskoka Bay, where the incidence of P. aeruginosa in water and sediment was found to be very low, P. aeruginosa was detected in only 0.38 percent of the ear swabs obtained from cottagers and no cases of otitis externa were encountered. At the beach at Gull Lake, however, P. aeruginosa was detected in the water and sediment and in the ears of swimmers much more frequently. On warm, sunny days when many swimmers were observed in the water, the density of P. aeruginosa in the water was found to increase significantly from early morning to midday. This increase was considered due mainly to direct and indirect contributions of fecal material from swimmers and to resuspension of P. aeruginosa from the sediments through

wave action and bather activity. At this site, P. aeruginosa was detected in 1.7 percent of the ear swabs from swimmers and 2 of the 68 participants contracted otitis externa during the period of study. A tendency was observed towards increased incidence of P. aeruginosa in ear swabs collected after daily swimming sessions compared to those collected before the sessions.

The results are similar to the findings of another study (Seyfried and Fraser, 1978) and provide further evidence of the potential health hazard posed by P. aeruginosa to users of recreational waters contaminated with this microorganism. Work on this topic will continue through 1978.

(K. Lautenschlager - (416) 248-3008).

## **FLUORIDE IN WATER AND WASTEWATER**

Fluoride ion in water is a subject of considerable interest due to its beneficial effects for man. Large amounts (up to 95%) of fluoride in water are absorbed by the body, and most of it is deposited in the bones and teeth. Long-term exposure to fluoride appears effective in preventing tooth decay and in reducing senile osteoporosis, especially in ageing women. However, excessive doses can result in tooth mottling.

Due to the narrow range between levels that are beneficial and those that can cause undesirable effects, a constant control of water fluoride levels is mandatory.

The manual colorimetric method includes a distillation step and is both dangerous and time-consuming. The automated version of the Alizarin-Fluorine Blue method eliminates these problems but requires complex instrumentation.

The advent of selective ion electrodes offered hope for a fast, simple, interference free method. Investigations to develop a method based on a fluoride specific electrode started in 1970, but performance problems were encountered. These were mainly due to mechanical

failures such as broken seals around the lanthanum crystal of the electrodes. Recently, electrode design has improved and the present probe appears to fulfill the stringent requirements of water analysis.

The method based on the fluoride specific electrode involves the buffering of the sample with a total ionic strength adjustment buffer (TISAB) and direct measurement of the fluoride concentration with the specific ion electrode using a three decimal pH meter. From the several TISAB formulae available Orion Research's EDTA-Acetate-Acetic Acid buffer was adopted. With this TISAB, the method is interference free between pH 5-9 except for aluminum from which a maximum of 1 mg/l may be tolerated.

In a comparison study on 200 routine samples analyzed by the two methods no significant differences were found, if the aluminum content remained below 1 mg/l. In industrial wastes with relatively high aluminum content,  $\text{AlF}_2^{2+}$  and  $\text{AlF}_2^+$  type complexes may form and a strong aluminum complexing agent is required. Experiments are underway to prepare such a complexing agent based on sulfosalicylic acid, EDTA and NaCl. This system requires a more stringent pH control. With satisfactory buffering and complexing, the method may be automated using Technicon's new ion specific electrode module as the heart of the system. This possibility will be examined in the next phase of the project.

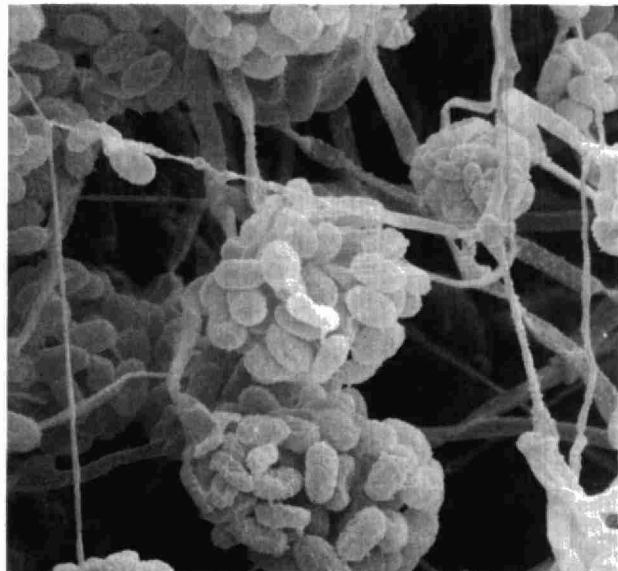
(M. Rawlings - (416) 248-3512)  
(R. Sadana - (416) 248-3346)

#### **PINPOINTING EMISSION SOURCES: CASE HISTORIES**

##### Microorganisms promote corrosion:

A complainant in Hamilton, Ontario claimed that his property was being damaged by emissions from steel and carbon black manufacturing industries in the area. Samples collected from the property by our field personnel were examined in the laboratory. Using an optical stereo microscope, the material in the sample was found to contain road dust (silica), graphite (from steel manufacturing), and black particles that had an appearance similar to

carbon black beads. However, using a polarizing microscope at high magnification and a scanning electron microscope, these beads were shown to be a fungus. The complainants were advised to use a household bleach to eliminate the problem.



##### Deposits on parked cars:

In an industrial park in the west end of Toronto, complaints were received regarding particulate emissions that had caused damage to about 300 new automobiles in the parking lot of an automobile dealership. Also, workers at a plant in the area complained of extreme physical discomfort caused by the emissions. Laboratory staff participated with field staff in an investigation to determine the source of the emissions. Samples were collected from the automobiles by brushing material from the surfaces and by means of adhesive tape.

Other samples were collected by exposing clear glass plates in and near the lot. Products from various manufacturing plants in the area were also obtained for comparison purposes. The samples were examined by optical microscopy and by electron microprobe analysis. The samples showed the presence of PVC and nepheline syenite, as well as individual particles containing sodium, together with silicon, chlorine, and sulphur. The PVC and nepheline syenite particles were traced back to a manufacturer of plastics, producing PVC using nepheline syenite as a filling

material. The sodium compounds were suspected to have come from a manufacturer of sodium silicate. Regional staff are conducting a survey of this plant to determine from which part of the process the emissions originated.

Source of filtering material in particulate matter:

A sample of black particulate matter, collected from a manhole in the sewer system in St. Catharines, was submitted for identification of the emission source. Examination of the material revealed the presence of coal particles and diatomaceous earth. Further investigations by field personnel revealed that the source of the material was a commercial recreation site, where the material was being used for filtering water to large fish tanks.



(J.A. Pimenta - (416) 248-7101).

**A FEASIBILITY STUDY FOR ANALYZING  
BOTH TOTAL SUSPENDED AIR  
PARTICULATES AND ASBESTOS ON  
THE SAME FILTERING MEDIUM**

Sampling methods and conditions are generally dictated by the requirements of the analytical procedure. In the case of the Total Suspended Air Particulates (TSAP) analysis, samples are collected by Hi-Vol samplers using a filtering medium with good flow characteristics and stable

uniform weight, such as mat type filters made from glass fibers. For asbestos analysis the above characteristics are not necessarily appropriate. Instead, the filters should be capable of being easily carbon coated, dissolved or incinerated in low temperature oxygen plasma furnaces. Membrane filters such as Nuclepore, Millipore, Gelman best conform to these requirements.

It is obvious that mat type filters are not suitable for a direct transfer asbestos method, while the membrane filters do not permit the sampling of sufficient amounts of air as required by TSAP determinations, since they easily clog, causing overheating of the Hi-Vol motor and/or rupture of filter. As a common filtering medium the Delbag Microsorban 98 filter was recommended due to its excellent flow characteristics.

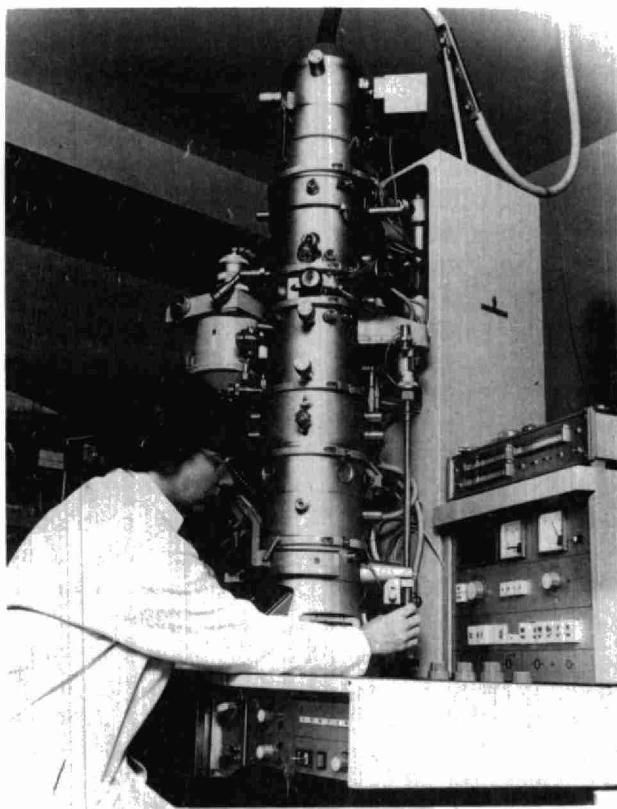
The Delbag filter as it is, is not suited for either of the two tests. For TSAP test it is too hygroscopic and tends to stick to the sampling device. The first problem may be solved with a preliminary moisture conditioning and preweighing of each filter. The second problem may be eliminated by using a Mylar adhesive tape around the edges of the filter.

For asbestos analysis the sample collected on Delbag should be transferred on another filter by using a solvent which dissolves Delbag but does not effect the other filter. Such solvents have been found. Delbag material is difficult to incinerate, as it is made from polystyrene fibers which under heating tend to further condense and carbonize. If EPA's direct transfer method is used, the Delbag filter should be dissolved and the suspension filtered through a Nuclepore filter, then the test is carried out as in the regular procedure. If incineration is required, the Delbag is dissolved, then the suspension filtered through a Sartorius cellulose nitrate filter, the filter burned, the residue resuspended and filtered through a Nuclepore filter and the test continued as usual.

As may be seen, several additional steps may be required to make use of the "one filter for two test" method. Since both air sampling and analysis are costly, the advantages and disadvantages of using Delbag filters should be evaluated with regard to saving of time and money in

sampling vs. the additional test costs due to a lengthier, more sophisticated analytical procedure.

(T. Pang - (416) 248-7161)



#### **RECOVERY OF ASBESTOS BY THE TEM METHOD FROM ARTIFICIAL ASBESTOS SUSPENSIONS**

The generally accepted method for the determination of asbestos fibres in the aquatic and atmospheric environment uses the transmission electron microscope (TEM). The aliquot obtained in a series of preparation steps and examined by TEM is but a very small fraction of the original sample. The use of statistical methods in counting and identification and large extrapolation factors could result in very large errors. At this time, the only assurance of the reliability of the results is the care the analyst takes in each step of the analysis. The analyst should make every effort to ensure uniform fibre distribution at each step from the sampling to the final counting. Since this is practically an impossible demand, the aliquots used should in each step be sufficiently large to reflect the actual concentration in the original sample when appropriate statistics are applied.

However, the truly meaningful way to validate the method is to run standards and determine the recoveries. Unfortunately, at this time, there is no method to prepare suspensions with a known number of asbestos fibres. However, we can weigh asbestos powder and prepare suspensions with known asbestos concentrations by weight. The recovery may be determined by calculating the mass of the fibres counted and sized and extrapolating the values to the original sample, then comparing the result with the amount expected to be present.

The problem with this method is that while the number of small fibres is much bigger, the large fibres have considerably more influence on the total mass. Due to the relatively small number of large fibres their distribution is less uniform and the error of extrapolation could be quite large especially when only the number of openings of the microscopic grid as required by the method are examined. The number of fibres thus counted might give a statistically valid result for the total number of fibres in the sample but with increasing error for the less abundant large fibres, and thereby for the total mass.

To overcome this difficulty, the laboratory has established a stratified counting procedure. First the fibres on the number of openings as required by the method are examined, then counting continues for fibres larger than  $5\mu$  until 50 fibres are found. In this way the mass of fibres less than  $5\mu$  in length and that of fibres larger than  $5\mu$  are determined separately. The sum of the two is compared to the known value of the original suspension, thereby determining the recovery.

Using this procedure the laboratory obtained recoveries ranging from 62% to 130%. Further refinement of the method may be obtained by establishing more than two size categories and extending counting for each category until a statistically meaningful number of fibres are counted. Further studies are required to evaluate the possibility of using artificial suspensions for spiking and applying the technique for the step by step evaluation of the various asbestos methods based on TEM.

(T. Pang - (416) 248-7101).

## ACTIVE TAGGING OF GASOLINES AND FUEL OILS WITH NITRO MUSK COMPOUNDS

Gasoline and fuel oil leakages from underground storage tanks are the most frequent causes of pollution by petroleum hydrocarbons in Ontario. In such cases, since minute quantities of these substances in drinking water can cause serious taste and odour problems, the prompt location and elimination of the pollution source is of great importance.

Several methods have been developed for the passive tagging of gasolines and fuel oils. Unfortunately, under environmental conditions petroleum hydrocarbon mixtures moving towards and in the aquifer often suffer alterations which make type-characterizations impossible after recovery for analysis.

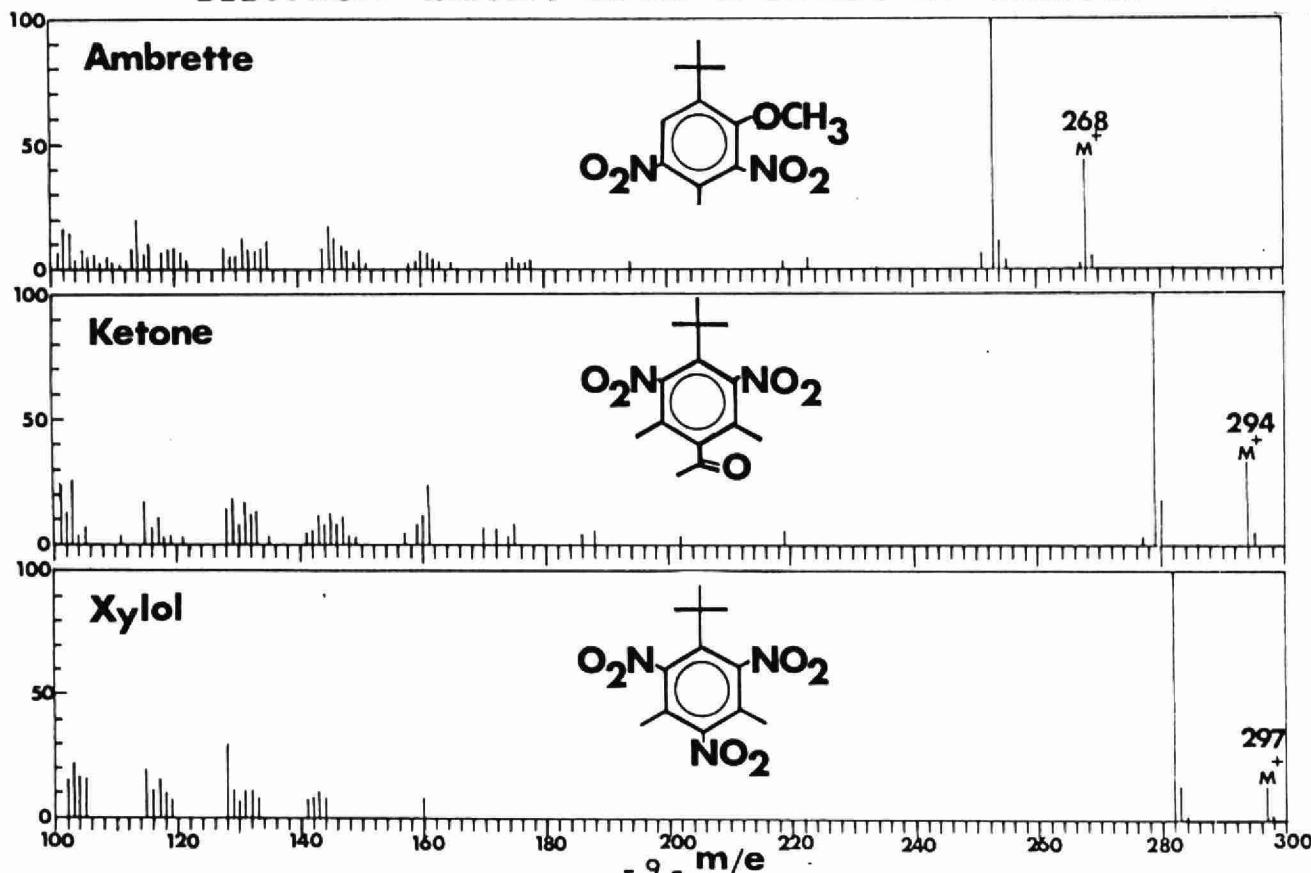
The choice of an active tagging agent for source identification involves a wide array of factors such as availability, compatibility with internal combustion engines, human toxicity, physical and chemical behaviour, stability and analytical detectability.

After these factors were considered, compounds classified as aromatic nitro

musks appeared to be very promising candidates as tagging agents. Musk-Xylool, Musk-Ketone and Musk-Ambrette were chosen for a feasibility study. The selection was based on the following properties: Nitro-musks are -

- readily available in high purity from suppliers of perfumery chemicals and at reasonable prices (\$4 - \$12 per lb.).
- they are on the "GRAS" (generally recognized as safe) list of chemicals and some are even permitted for use in flavour compositions.
- they show good solubilities in gasoline (2-12%), more than adequate for the intended purpose.
- they promised good specific detectability by GC-electron capture detectors (nitro-groups).
- they promised specific detectability by nitrogen specific detectors (AFID).
- they promised low leachability by water (partition coefficients between 900 ml water and 100 ml gasoline were found to be between 1:40,000 and 1:263,000).
- they are known to be good "fixatives" not easily lost by evaporation.

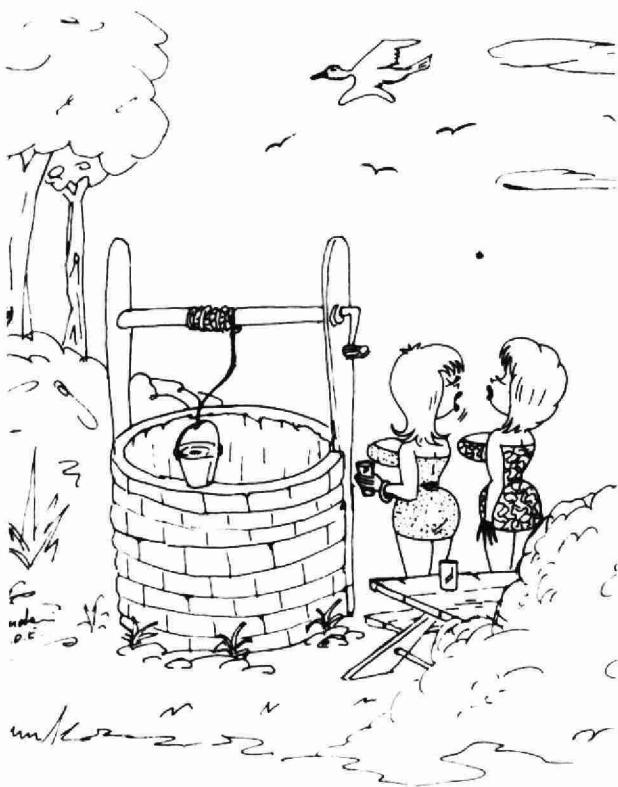
## ELECTRON IMPACT MASS SPECTRA OF 3 MUSKS



Test runs carried out with an internal combustion engine using gasoline heavily dosed with musks (500 ppm) did not indicate any impairment; if anything the addition of musks improved exhaust quality.

Detection limits were determined and ranged from 1 ng by gas chromatography-flame ionization detector down to 10 pg using GC-alkaline-flame ionization detector when pure standards were used. In the case of field samples which may contain interfering components GC-MS can be used with selective ion monitoring.

The recommended dosage for tagging is 10-100 ppm. So far, two field trials have been carried out and both were satisfactory. In one case, three underground gasoline tanks were tagged simultaneously and two were found to be leaking. The second case involved a fuel oil tank where earlier pressure tests were inconclusive.



"Well, maybe you can't drink it, but it makes a great perfume!"

The laboratory is continuing work in this direction to add further compounds to our repertoire of tagging agents. Field personnel would like to be able to use as many as six markers simultaneously.

(O. Meresz - (416) 248-3031).

## ONE STEP CONVERSION OF TRIGLYCERIDES TO FATTY ACID METHYL ESTERS

The determination of fatty acid distribution pattern of triglycerides can be very important in source identification work. The conversion of fats and oils into fatty acid methyl esters for gas chromatographic analysis is usually effected by saponification, extraction of free fatty acids after acidification, followed by evaporation and esterification using diazo methane in ethyl ether.

The results of a feasibility study carried out in our laboratory indicate that this tedious route can be replaced by a simple one-step transesterification using methanol and commercial sodium methoxide as the catalyst. Application of an excess of sodium methoxide allowed the use of reagent grade methanol and eliminated interference by free fatty acids.

Typically, 100 mg of a fat or oil sample is taken up in methanol (10-15 ml), sodium methoxide (0.1 - 0.2 g) is added and the mixture is stirred on a magnetic stirrer overnight at room temperature in a stoppered Erlenmeyer flask. The transesterification can conveniently be followed by TLC using silica gel microplates. When the reaction is completed, solid sodium bicarbonate (0.1 - 0.2 g) is added and stirring continued for an additional two-hour period. The mixture is then filtered and the filtrate is evaporated and made up with methanol to standard volume for analysis. Alternatively, the mixture can be taken to dryness and the residue taken up in cyclohexane.

The method is also applicable to samples contaminated with mineral oil or non-saponifiable lipids. Gas chromatographic analysis before and after transesterification will show any interference by non-fat components during the final analysis.

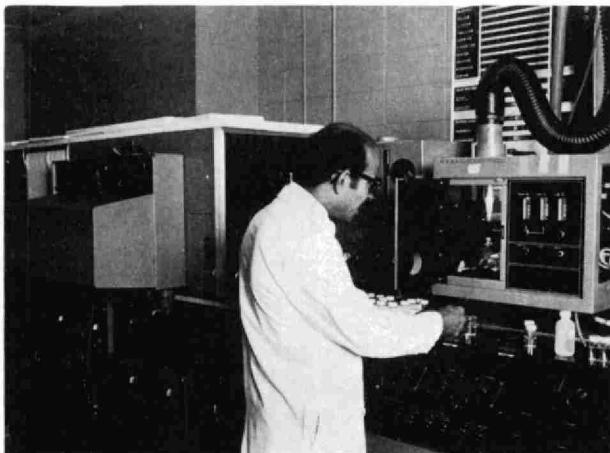
(O. Meresz - (416) 248-3031).

## RESURRECTION OF EMISSION SPECTROSCOPY

Emission spectrography is one of the techniques capable of providing the multi-elemental analysis often required for environmental monitoring. The advent of the inductively coupled plasma torch (ICPT) has significantly increased the sensitivity, accuracy and precision of emission spectrographic analysis and has established many applications for useful diagnostic work in an environmental laboratory.

The ICPT replaces conventional energy sources such as the electrical arc or spark, and like these sources, has the purpose of creating excited atoms of each element comprising the sample. These excited atoms lose their energy in the form of emitted light energy, and since the wavelength of light emitted is unique for each element, and its intensity is proportional to the number of atoms emitting, the constituent elements and their concentration in the sample can be determined.

The ICPT is comprised of a quartz torch surrounded by an induction coil. The plasma is initiated by generating a cloud of electrons which inductively couple with the coil energy, creating a flamelike plasma. Argon is introduced into the torch to cool the quartz, to stabilize the plasma, and to introduce the sample to the energy of the plasma.



The sample is aspirated into an aerosol generator, and the aerosol is carried by argon into the plasma, where the following sequence of events occurs:

- desolvation of aerosol
- dehydration of aerosol
- vaporization
- atomization
- excitation of atoms

The blend of spectra thus obtained is characteristic of all the elements comprising the sample.

The MOE laboratory has acquired an ICPT as the source for its convertible spectrometer system. This system can be used either in its direct-reading or photographic plate modes of spectral recording. The system is based on a convertible 3.4 meter Ebert-type spectrograph-direct reading spectrometer.

The photographic plate mode, while somewhat time-consuming, is used in a diagnostic capacity to alert the client to the possible presence of unsuspected trace metals. It is also invaluable in developing wide ranging baseline data which can be reviewed in future years to assess changing trends.

The Direct Reading Mode involves the monitoring of the spectral line signals from a predetermined number of elements by dedicated computer controlled photomultiplier tubes. The computer correlates the accumulated signals of all the analytical channels using the standardized calibration curves, and corrects for interferences prior to tabulation of the final results.

The main applications to date have been in quantitative sediment trace metal analysis, in routine water analyses. Exploratory work is being carried out using ICPT for metal scans of vegetation affected by atmospheric fallout and for the analysis of air particulates collected by high volume air filters.

(M. Moseley - (416) 248-3029).

### ONE PART PER BILLION

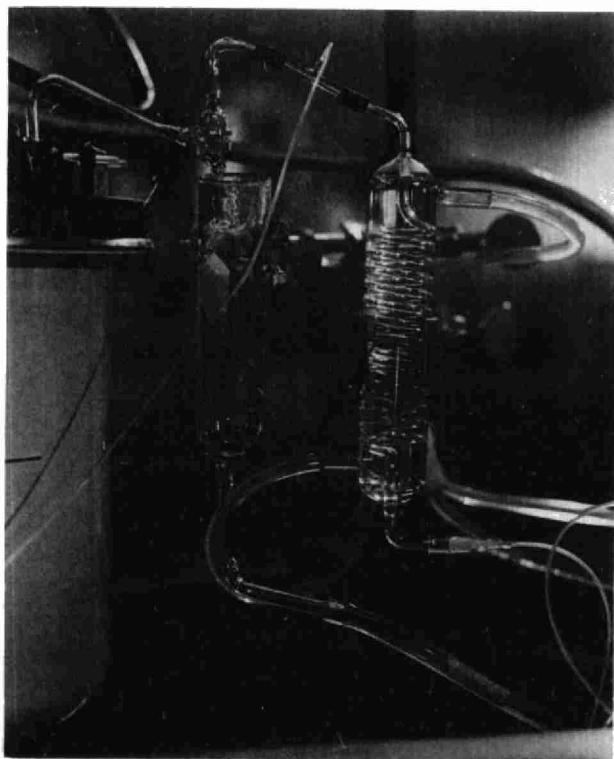
Analysts commonly use the term "part per billion".

We all know that it is a small amount, but just how small is it, in the real world?

- 1 second out of 72 years
- a 1 gram needle in a 1000 ton haystack
- 1 penny out of \$10,000,000
- the first centimeter of a 6200 mile trip
- one shot of wormhole in a 78,000 ton (very dry) martini
- 1 maxwell out of 10 webers.

## AUTOMATED DISTILLATION TECHNIQUE FOR DETERMINATION OF AMMONIA IN WATER AND WASTE WATER SAMPLES

An automated distillation system has been developed and synchronized with indophenol blue colorimetry to determine the ammonia concentration of water samples which are not amenable to a colorimetric procedure unless pre-treated. Samples are buffered, distilled and a portion of the resultant ammonia vapour is mixed with hydrochloric acid prior to condensation and colorimetric measurement. The calibration for the system is linear and designed for the range 0-0.5 mg/l; higher concentration ranges are obtained by dilution. The precision, which was estimated by analyzing routine samples in duplicate, indicated a standard deviation of 0.005 mg/l N at the 0.2 mg/l N level; twenty samples per hour may be analyzed.



The precision and rate of analysis are superior to those obtained using the standard manual distillation procedure. This system has been used in determining the ammonia concentrations of mining, tanning, slaughterhouse and ammonia stripping tower wastes.

(J. Crowthers - (416) 248-3512).

## IDENTIFICATION OF VOLATILE ORGANICS OF INDUSTRIAL ORIGIN IN TAINTED FISH TISSUE

Studies of fish tainting caused by organic pollutants have largely been carried out by tasting panels. Little work has been done to identify and quantitate the compounds involved, because attempts to extract and analyze the problem chemicals often lead to difficulties due to interferences by the large quantities of biological materials, such as lipids and cholesterol, which are also extracted. We have successfully applied a purging technique, developed originally to analyze volatile organics in water, to separate the odour and taste causing substances from fish tissue.

The apparatus used consists of a glass bottle with a fritted bottom, a nitrogen inlet beneath the frit and an outlet near the top of the bottle. The outlet is fitted with a stainless steel tube containing Tenax GC and SP2100 to trap organic compounds. A small quantity (10-30 gm) of homogenized fish tissue and 100-200 ml of purified, distilled water are added to the bottle, which is then placed in a water bath. A flow of nitrogen, 10-15 ml/minute, is maintained through the bottle for 20-30 minutes after which the trap is transferred to the gas chromatograph of a combined gas chromatograph-mass spectrometer system for analysis. A 4-port valve is used to allow the trap to be bypassed or included in the carrier gas flow. Desorption of the organics occurs as the GC oven is heated. Typically a 2 ft. Chromosorb 101 GC column is used, run isothermally at 50°C for 4 minutes and then programmed to 210°C at 6-12°C/minute. The compounds detected depend on the purging temperature, e.g. at 80°C compounds of limited volatility such as naphthalene may be quantitatively purged. The sensitivity of the method allows detection and quantitation at low ppb levels.

Currently we are analyzing a series of fish samples by this method in an attempt to correlate the compounds present with some earlier results from a panel of tasters. Thus far, the following volatile organic compounds have been isolated from fish tissue and identified by GC/MS:

Aliphatic hydrocarbons, Benzene, Chloroform, Dichlorobenzene, ethyl toluene, isopropylbenzene, Methylnaphthalene, Naphthalene, n-propylbenzene, Styrene, Tetrachloroethylene, Tetramethylbenzene, Toluene, Trichlorobenzene, Trichloroethylene, Trimethylbenzene, Xylenes.

(R.F. Bonner - (416) 248-3031).

#### MERCURY AND GOLF COURSES

Approximately 50% of golf courses in Ontario use some form of mercurial fungicide on greens, aprons and tees for the control of a number of grass diseases. The forms of mercury used are mercurous chloride, mercuric chloride and phenylmercuric acetate. The annual application of these compounds to golf courses across Canada amounts to an estimated three tons of mercury.

Typically, the fungicide is applied to the greens in late November or early December, prior to the first major snowfalls, to prevent the damage caused by pink and grey snow moulds. Staff from the Water Resources Branch of the Ministry studied two golf courses in the Toronto area, taking water, grass and soil core samples from greens, fairways, and rough areas before and after the fungicide application.

The samples from the rough and fairways showed little change before and after the fungicide application to the greens. (Most golf courses only apply the mercury compounds to greens because of cost). The grass on the greens showed a large increase in mercury levels (from 7 to 1500 ppm in one case, from 50 to 2300 ppm in the other). The significance of the application of mercurial fungicides to golf greens, particularly with regard to percolation into water bodies, is not known, but studies are being planned to assess this. One U.S. study indicated that most of the mercury applied to the greens is retained in the top six inches of the soil, but evaporative losses were not measured.

One conclusive result of this brief study was that worms living on golf courses accumulate significant levels of mercury.

Some worms contained over one hundred ppm mercury well in excess of the 0.5

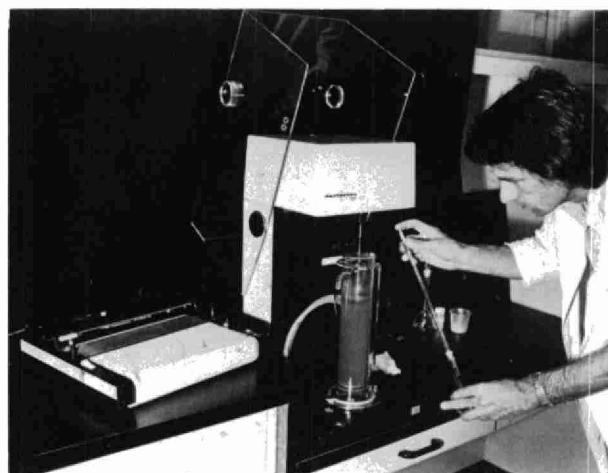
ppm level recommended for unrestricted consumption of worms.

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(A. Johnson - (416) 248-5954).

#### PARTICLE SIZE ANALYSIS

The Air Quality Section now has the capability of performing particle size analysis on very small sediment and soil samples. Previously, at least 5 grams of material was required for such analyses, and the material thus analyzed could always be used for further analyses.

The newly acquired automated sedimentation balance can routinely determine particle size distributions on samples as



small as 0.1 g, although 0.3 to 1.5 g is preferred, in the 1 to 150 um size range of particles. Operating on the classical sedimentation principle, a time versus weight of sedimented material curve is automatically generated when the material, previously suspended in a liquid, is collected on a pan located near the bottom of a cylinder. From this record, a particle size distribution can be calculated based upon Stoke's law of spheres falling through a viscous liquid.

Application lends itself to those samples which are difficult to collect in large quantities (such as suspended sediments). Furthermore, the samples can now be analyzed for particle size distribution without sacrificing other equally important parameters.

(J.F. Hipfner - (416) 248-3346).

## FOUNDRY SANDS AS POTENTIAL SOURCES OF ENVIRONMENTAL PHENOL CONTAMINATION

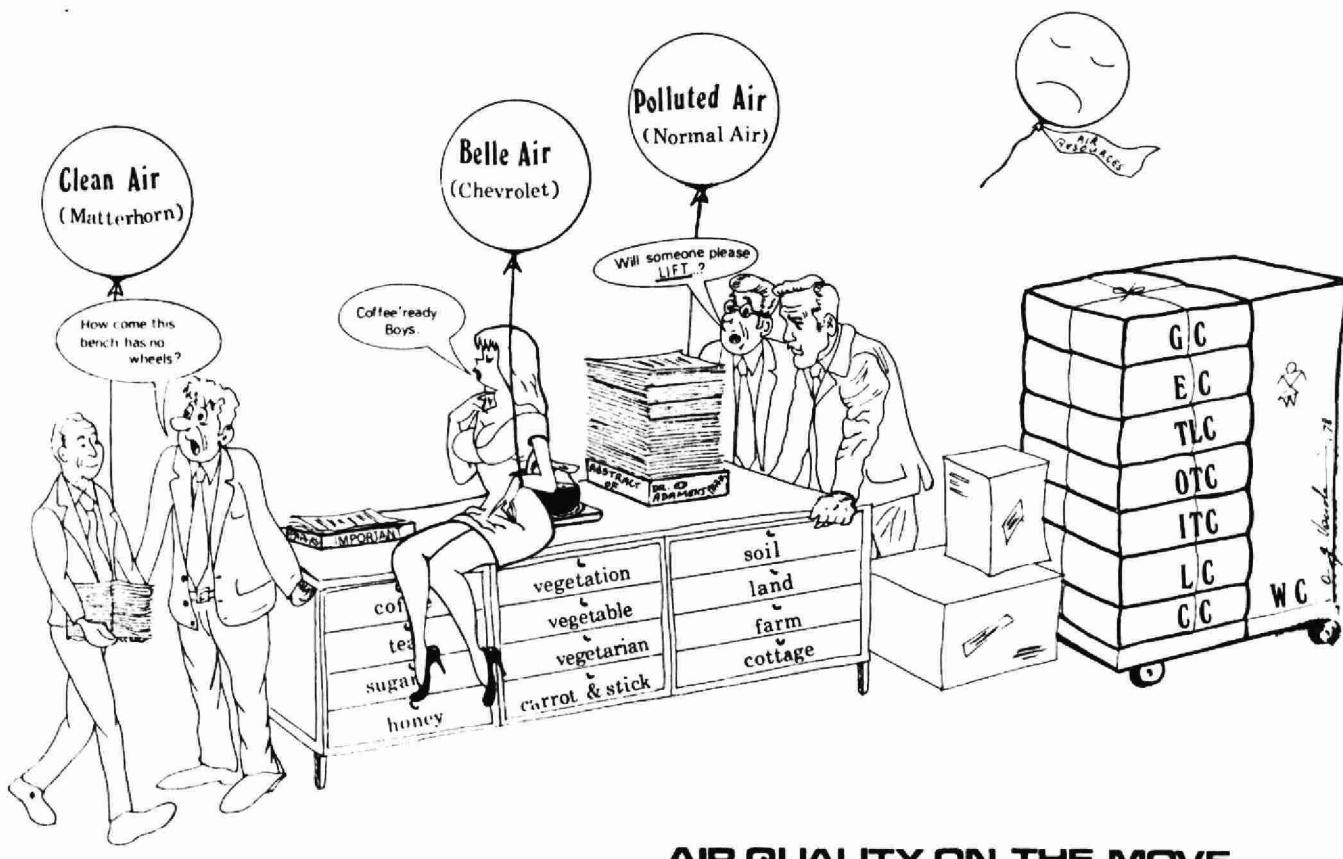
The by-products of foundry operations, spent and waste foundry sands can accumulate in tonnage quantities and their disposal can present serious environmental problems. Faced with the question whether landfilling might be a suitable method for foundry sand disposal, our laboratory carried out a preliminary study on phenol release potential of a variety of foundry sands.

Leachability under natural conditions was simulated using distilled water and the total phenol release potential was estimated by leaching experiments using 1%

aqueous potassium hydroxide. Total leached phenols were determined using the Gibbs method or the automated 4-amino-antipyrine technique.

Of the 12 samples analyzed, phenol concentrations varied between 60 ug/kg and 290 mg/kg of dry sand. Seven samples showed no difference in phenol content obtainable with distilled water or KOH, respectively, while five samples released about ten times as much phenol with KOH than with distilled water. Burned and used sands exhibited the lowest phenol release potentials (0.06 - 3.0 mg/kg). It was recommended that the waste sand be burned before disposal.

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AIR QUALITY ON THE MOVE

## RECENT PAPERS AND REPORTS PREPARED BY LABORATORY STAFF

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M. Young, Comparison of Media for Heterotrophic Plate Counts from Surface Waters. Presented at the 28th Annual Meeting of the Canadian Society of Microbiology, June, 1978 in Montreal, Canada.

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A.B. Foster, R.A. Clarke, Development and Analysis of a Short Time Period Method for Determination of Lead in Air Particulates.

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D. Boomer, Computer Program for Semi-Automated Analysis of Spectrographic Plates.

P.N. Vijan, Determination of Arsenic in Urine.

P.N. Vijan, C. Chan, Semi-Automated Determination of Antimony in Rocks.

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# analysis

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